

Standard Operating Procedure for the Analysis of 1,2-Dibromoethane (EDB), 1,2-Dibromo-3-Chloropropane (DBCP) and 1,2,3-Trichloropropane (123TCP) in Water by Microextraction and Gas Chromatography

1.0 Scope and Application

- 1.1 This method is applicable to the determination of 1,2-Dibromoethane (EDB), 1,2-Dibromo-3-Chloropropane (DBCP) and 1,2,3-Trichloropropane (123TCP) in drinking water and ground water.
- 1.2 The experimentally determined method detection limits (MDL) for EDB and DBCP were calculated to be 0.01 ug/L and the MDL for 123TCP was calculated to be 0.02 ug/L. The method has been useful for these analytes over a concentration range from approximately 0.03 to 200 ug/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2.0 Summary of Method

- 2.1 Thirty five mL of sample are extracted with 2 mL of pentane. Five uL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and detection. Analytes are quantitated using external procedural standard calibration.
- 2.2 Confirmatory evidence should be obtained for all positive results. This data may be obtained by using retention data from a dissimilar column, or when concentrations are sufficiently high, by GC/MS. Purge and trap techniques using EPA Methods 502.2 and 524.2 may also be used. Confirmation of all positive results of EDB are especially important because of the potential for misidentification of dibromochloromethane (DBCM) as EDB.

3.0 Definitions

- 3.1 Laboratory Reagent Blank (LRB) - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.2 Field Reagent Blank (FRB) - An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions,

storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

- 3.3 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.4 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentration.
- 3.5 Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.6 Primary Dilution Standard Solution (PDS) - A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.7 Calibration Standard (CAL) - A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.8 Procedural Standard Calibration - A calibration method where aqueous calibration standards are prepared and processed (e.g., purged, extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analysis are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.
- 3.9 Quality Control Sample (QCS) - A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with

externally prepared test materials.

4.0 Interferences

- 4.1 Impurities in the extracting solvent usually account for the majority of the interferences. Solvent blanks should be analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the reagent water blanks. Whenever an interference is noted in the reagent water blank, the analyst should reanalyze the extracting solvent. It is generally more economical to obtain a new source of solvent rather than attempting purification. Interference-free solvent is defined as a solvent containing less than the MDL of an individual analyte interference. Interference-free solvents should be protected by storing in an area free of organochlorine solvents.
- 4.2 This liquid-liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds, and in addition extracts polar organic components of the sample with varying efficiencies.
- 4.3 Dibromochloromethane (DBCM) is a common disinfection byproduct in chlorinated drinking waters that frequently occurs at relatively high concentration. DBCM can elute very close to EDB, and a high concentration of DBCM may mask a low concentration of EDB or be misidentified as EDB. Therefore, special care should be taken in the identification and confirmation of EDB.
- 4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be limited. Material Safety Data Sheets are maintained in the laboratory for chemicals used in this method.
- 5.2 EDB, DBCP, and 123TCP have all been tentatively classified as known or

suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 Equipment and Supplies

- 6.1 Sample containers - 40 mL screw cap amber vials each equipped with a Teflon-lined cap. Individual vials shown to contain at least 40.0 mL can be calibrated at the 35.0 mL mark so that volumetric, rather than gravimetric measurements of sample volumes can be performed. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area free of organic solvent.
- 6.2 Vials, autosampler, screw or crimp cap with Teflon faced septa, 1.8 mL.
- 6.3 Pipettes
 - 6.3.1 Microliter adjustable (0-100 uL)
 - 6.3.2 Volumetric (2.0 mL)
 - 6.3.3 Disposable Pasteur (5 & 3/4" or 9")
- 6.4 Top loading balance capable of weighing to the nearest 0.01 gram
- 6.5 Amber glass vials with Teflon-lined screw caps for standard storage
- 6.6 Volumetric flasks (glass stoppered) class A - 5, 10, 100, and 200 mL
- 6.7 Gas chromatography system with autosampler - The gas chromatograph must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column split/splitless injector. This laboratory uses a Hewlett Packard 5890 GC.

7.0 Reagents

7.1. Extraction solvent

Pentane has been found to be a suitable extraction solvent for this analysis. However, the solvent must be demonstrated to be of a satisfactory purity before it

can be used for this method. Therefore, solvent blanks must be analyzed on each new bottle of solvent before use. Interference-free solvent is defined as a solvent containing less than the MDL of an individual analyte interference. Aldrich THM Grade pentane (Catalog No 41,480-8) has been found to be suitable, but each lot must be analyzed to confirm that it is suitable. Protect interference-free solvents by storing in an area free of organochlorine solvents.

- 7.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of method analytes above the MDLs.
- 7.3 Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, ACS Reagent Grade - prepare a 40 mg/mL solution in reagent water.
- 7.4 Reagent water
 - 7.4.1 Definition - Water free of interferences above the analyte MDLs
 - 7.4.2 Preparation - In this laboratory reagent water is prepared by passing reverse osmosis water through a Barnstead Nanopure system.
 - 7.4.3 Testing - Test reagent water each day it is used by extracting and analyzing it as you would a standard or sample.

8.0 Sample Collection, Preservation, and Storage

8.1 Sample collection

- 8.1.1 Replicate field reagent blanks (FRB) must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample vials with reagent water, seal, and ship to the sampling site along with sample vials. Whenever a set of samples is shipped and stored, it must be accompanied by the FRB.
- 8.1.2 Collect all samples in 40 mL vials into which 3 mg of sodium thiosulfate crystals have been added just prior to shipping to the sampling site. Alternately, 75 μL of freshly prepared sodium thiosulfate solution (40

mg/mL) may be added to empty 40 mL vials just prior to sample collection. This dechlorinating agent must be added to each sample to avoid the possibility of reactions that may occur between residual chlorine and indeterminate contaminants present in some solvents, yielding compounds that may subsequently interfere with the analysis. The presence of sodium thiosulfate will arrest further formation of DBCM.

- 8.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. There must be no head space in the filled sample vials once they are capped.
- 8.1.4 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill 40 mL sample vials. As above, there must be no head space in the filled sample vials once they are capped.

8.2 Sample preservation

The samples must be chilled to 4°C or less at the time of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be ≤4°C on arrival at the laboratory.

8.3 Sample storage and holding time

- 8.3.1 Store samples and field reagent blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors.
- 8.3.2 Because 1,2,3-trichloropropane has been added to the analyte list in this method and has been found to have a 14 day maximum holding time in studies conducted for EPA Method 524.2, all samples must be extracted within 14 days of collection. Samples not analyzed within this period must be discarded and recollected. Because of the potential for solvent evaporation, it is preferred that extracts be analyzed immediately following preparation. When necessary, extracts may be stored in tightly capped vials at 4°C or less for up to 24 hr.

9.0 Initial Demonstration of Capability

- 9.1 Initial demonstration of capability - The analyst must make an initial

determination of the method detection limits and demonstrate the ability to generate acceptable precision with this method.

- 9.1.1. Prepare four to seven LFBs at a concentration equal to 10 times the MDL or at a concentration in the middle of the established calibration range.
- 9.1.2 Extract and analyze the LFBs according to the procedure in section 11.
- 9.1.3 Calculate the mean concentration found (X) in ug/L, and the standard deviation of the concentrations in ug/L, for each analyte.
- 9.1.4 For each analyte, X should be between 70% and 130% of the true value. The RSD should be 20% or less. If the results for all three analytes meet these criteria, the system performance is acceptable. If any analyte fails to meet the criteria, correct the source of the problem and repeat the test.
- 9.1.5 Determination of MDL. Prepare four to seven LFBs at a low concentration. Use the concentrations in Tables 1 and 2 as a guideline, or use calibration data to estimate a concentration for each analyte that will produce a chromatographic peak with a 3-5 signal to noise ratio. It is recommended that LFBs for determination of the MDL be prepared and analyzed over a period of several days so that day to day variations will be reflected in the precision data.
- 9.1.6 Analyze the LFBs according to the procedure in section 11. Calculate the mean amount recovered and the standard deviation of these measurements. Use the standard deviation and the following formula to calculate the MDL.

$$MDL = S t_{(n-1, 1-\alpha = 0.99)}$$

where:

$t_{(n-1, 1-\alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses

10.0 Standard and Quality Control Preparation

10.1 Standard Preparation

10.1.1 Stock Standard Solutions

Multicomponent concentrates are commercially available. The commercial standard this laboratory normally uses is Catalog Number 4-8225 from Supelco. This standard is at a concentration of 2000 ug/mL 1,2-dibromomethane and 1,2-dibromo-3chloropropane in methanol.

10.1.2 Intermediate Solution Preparation

One intermediate solution, Intermediate 1 (I1) must be prepared for use in standard preparation. Be sure that the solution has not passed it's expiration date.

Procedure: Using a 10uL syringe, dilute standard stock 10uL/10mL in methanol

$$2000 \text{ ug/mL} \times 0.01\text{mL}/10\text{mL} = 2.0 \text{ ug/mL each EDB and DBCP}$$

10.1.3 Calibration Standard Preparation

10.1.3.1 Number and concentration range

At least three calibration standards are needed; five are recommended. A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 use at least five standards. The lowest standard should represent analyte concentrations near the respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts or should define the working range of the detector. Normal procedure in this laboratory is to prepare 7 calibration standards in the concentration range of 0.005 - 0.40 ug/L.

10.1.3.2 Using a 25uL syringe, prepare the calibration standards in water using I1 as follows:

| <u>Standard</u> | <u>Dilution</u> | <u>Concentration</u> |
|-----------------|-----------------|----------------------|
|-----------------|-----------------|----------------------|

| | | |
|------------|-----------------|------------|
| Standard 1 | 0.5uL I1/200mL | 0.005 ug/L |
| Standard 2 | 1.0uL I1/200mL | 0.010 ug/L |
| Standard 3 | 2.0uL I1/200mL | 0.020 ug/L |
| Standard 4 | 5.0uL I1/200mL | 0.050 ug/L |
| Standard 5 | 10.0uL I1/200mL | 0.10 ug/L |
| Standard 6 | 20.0uL I1/200mL | 0.20 ug/L |
| Standard 7 | 20.0uL I1/100mL | 0.40 ug/L |

Example calculation of concentration: Standard 4

$$2.0 \text{ ug/mL} \times 0.005\text{mL}/0.20\text{L} = 0.05 \text{ ug/L}$$

10.2 Quality Control Sample Preparation

The minimum quality control requirements for each sample analysis set consist of the determination of adequate resolution of dibromochloromethane and EDB, the analysis of field reagent blanks (FRB), laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified matrix (LFM), standards containing low levels of each analyte, and quality control samples (QCS) to evaluate and document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. In recognition of advances that occur in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the initial demonstration of capability.

10.2.1 Dibromochloromethane/EDB resolution check

Dibromochloromethane (DBCM) is a common disinfection byproduct in chlorinated drinking waters that frequently occurs at relatively high concentrations. DBCM can elute very close to EDB, and a high concentration of DBCM may mask a low concentration of EDB or be misidentified as EDB. A check must be done to ensure that there is adequate separation between a high concentration of DBCM and a low concentration of EDB. One way to accomplish this is to spike a low level

EDB/DBCP standard (0.01 ug/L) with a concentration of DBCM at the highest level anticipated in any sample to determine if resolution is adequate to detect EDB under the worst case conditions. The resolution solution preparation is as follows

Prepare a 0.01 ug/L standard - See Section 10.1.3.2

To the same 200mL volumetric flask add: 20uL Trihalomethane Standard Stock, Supelco Product Number 48746. Concentration of DBCM in this stock solution is 200ug/mL

DBCM concentration = $200 \text{ ug/mL} \times 0.02\text{mL}/0.20\text{L} = 20 \text{ ug/L}$

Ideally, this solution is extracted and analyzed before the rest of the samples to ensure adequate resolution of DBCM and EDB.

See Section 11 for extraction procedure.

Chromatogram 1 in Section 17 demonstrates acceptable resolution of DBCM and EDB.

10.2.2 Analysis of field reagent blanks.

Field reagent blank (FRB) must be analyzed to determine if method analytes or other interferences are present in the field environment. Background interferences co-eluting with method analytes should be below the method detection limits. See Section 11 for extraction procedure.

10.2.3 Analysis of laboratory reagent blanks

With each extraction set the analyst must analyze a laboratory reagent blank (LRB) to demonstrate that interferences from the analytical system are under control before any samples are analyzed. Background interferences co-eluting with method analytes should be below the method detection limits.

10.2.4 Analysis of laboratory fortified blanks

The analyst must demonstrate that the measurement system is in control by analyzing laboratory fortified blanks (LFB's) of the analytes at concentrations of 0.05 ug/L and 0.25 ug/L. This must be demonstrated at a frequency equivalent to 10% of the sample load, or 1 per batch of samples

extracted, whichever is the greater frequency.

10.2.4.1 Stock LFB Solution

Multicomponent concentrates are commercially available. The commercial standard this laboratory normally uses is Catalog Number 4-8225 from Supelco. This standard is at a concentration of 2000 ug/mL 1,2-dibromomethane and 1,2-dibromo-3-chloropropane in methanol. **Note:** This must be a different vial from the standard vial.

10.2.4.2 Intermediate Solution Preparation

One intermediate solution, Intermediate 1 (I1) must be prepared for use in standard preparation. Be sure that the solution has not passed its expiration date.

Procedure: Using a 10uL syringe, dilute standard stock 10uL/10mL in methanol

$2000 \text{ ug/mL} \times 0.01\text{mL}/10\text{mL} = 2.0\text{ug/mL}$ each EDB/DBCP.

10.2.4.3 LFB Solution Preparation

Using the same 25uL syringe used to prepare the standards, prepare the 0.05 and 0.25 ug/L LFB's in water as follows:

| <u>LFB</u> | <u>Dilution</u> | <u>Concentration</u> |
|------------|-----------------|----------------------|
| 0.05 ug/L | 5uL I1/200mL | 0.05 ug/L |
| 0.25 ug/L | 12.5uL I1/100mL | 0.25 ug/L |

Example calculation of LFB concentration:

$2.0 \text{ ug/mL} \times 0.005\text{mL}/0.20\text{L} = 0.05 \text{ ug/L}$ each EDB/DBCP.

See Section 11 for extraction procedure.

Extract and analyze with the samples. Recovery must be between 70 and 130%.

10.2.5 Preparation of laboratory fortified matrix

At least once in every 20 samples, fortify an aliquot of a randomly selected routine sample with known amounts of the analytes to assess matrix effects. The added concentration should not be less than the background concentration of the sample selected for fortification. Procedure is as follows:

Using the 25uL syringe, add to 35 mL of the sample:

4uL LFB I1

Analyte concentration =

$$2.0 \text{ ug/mL} \times 0.004\text{mL}/0.035\text{L} = 0.23 \text{ ug/L}$$

Extract and analyze with the samples. Recovery should be between 70 and 130%.

See Section 11 for extraction procedure.

10.2.6 Assessing analyte sensitivity

The analyst should demonstrate the ability to analyze low levels of each analyte.

Prepare 0.02 ug/L (the method MDL) standard. See Section 10.1.3.2

Extract and analyze the sample.

The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If it is not, correct the problem and repeat the test.

Calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst should repeat the test for that analyte. Repeated failure, however, will confirm a general problem with the measurement system or faulty standards. If this occurs, locate and correct the source of the problem and repeat the test.

10.2.7 Quality control sample

At least quarterly, a quality control sample should be analyzed. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the source of the problem. This laboratory normally analyzes a quality control sample each time samples are analyzed.

- 10.3 It is recommended that additional quality control practices be adopted for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the measurements. Whenever possible, standard reference materials should be analyzed. This laboratory participates in relevant proficiency test studies on an annual basis.

11.0 Extraction Procedure

Note: Before extracting and analyzing any samples, analyze a portion of the extraction solvent to determine if it is acceptable for extraction and analysis of standards and samples. If the extraction solvent contains any detectable peaks within the retention time window for any of the method analytes, it is unsuitable.

- 11.1 Remove samples and field reagent blanks from storage and allow them to warm to room temperature.
- 11.2 Sample volume is determined by weight. Weigh 35 grams of each standard, quality control sample, and field sample into separate 40 mL vials.
- 11.3 Add 2.0 mL pentane to the first vial to be extracted. Shake the vial for 2 minutes. Allow the phases to separate while shaking the next vial.
- 11.4 After the phases separate, transfer the pentane phase to an autosampler vial for analysis. Be careful not to transfer any water along with the pentane.

12.0 Data Analysis, Calculations, and Reporting

12.1 Typical operating parameters

Column: RTX-VRX, 60 meter x 0.25 mm ID; 1.4 u film thickness

Column maximum temp: 260 degrees C

Temperature program:

40 degrees C for 0 minutes

3 degrees C/min to 115 degrees C, hold for 23 min (48min)

35 degrees C/min to 230 degrees C, hold for 10 min (13.3min)

Acquisition time: 3800 seconds = 63.33 minutes

Inlet: Liner = Supelco Steel at 210 degrees C

Injection volume: 5 uL

Purge: Initial = off; On at 0.50 minutes

Column Head Pressure: 15 psi

Make-up gas flow to ECD = 45 mL/min

Detector: ECD A at 300 degrees C

12.2 X-Chrom data acquisition system is used in our laboratory. Integrate the blank, sample, and quality control check chromatograms and review the integration to ensure that peak detection and integration was performed acceptably. Process these chromatograms to identify peaks and quantitate and report results.

12.3 Calculated the corrected sample concentration as:

$$\text{Concentration, ug/L} = C_i \times (35/V_s)$$

Where: C_i = uncorrected concentration

V_s = sample volume

Or incorporate this calculation as one of the user equations in the chromatography data system method file.

12.4 Evaluate the quality control check results to ensure that they are within acceptable limits.

12.5 Enter the results into the Laboratory Information Management System (LIMS).

- 12.6 Using the conditions set forth in this SOP, results of the most recently completed annual check sample study are detailed here.

Method file: edbdbcp20020307jeq
Analysis file: edbdbcp20020307jeq

Sample 02-Q104

Sample directions are to dilute 20uL to 100mL water. This frequently yields analyte levels higher than the highest calibration level, so dilutions of 2uL, 5uL, and 10uL to 100mL water are also prepared.

Extraction date: 03/06/02
Analysis date and time: 03/08/02 0740
File 19 of the analysis
Results are from the 2uL dilution

| | True Value | Recovery |
|---|------------|----------|
| EDB result: $0.118 \text{ ug/L} \times 20/2 = 1.18 \text{ ug/L}$ | 1.01 ug/L | 117% |
| DBCP result: $0.168 \text{ ug/L} \times 20/2 = 1.68 \text{ ug/L}$ | 1.51 ug/L | 111% |

Chomatogram 2 in Section 17 demonstrates a typical chromatogram of an EDB/DBCP standard injection.

13.0 Method Performance

Single laboratory accuracy and precision data are presented for the three method analytes in reagent water at concentrations of 0.1 ug/L and 0.2 ug/L as generated by the developers of EPA Method 504.1. Table 1 lists the data generated using Column A from the EPA method and Table 2 lists data generated using column B from the EPA method. The method detection limits in the table were calculated using the formula from section 9.1.1.6.

14.0 Pollution Prevention

This method uses a microextraction procedure that uses very small volumes of solvent.

Thus, the method is quite safe for use by the analyst and harmless to the environment. For information concerning pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society.

16.0 References

16.1 "1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) and 1,2,3-Trichloropropane (123TCP) in Water by Microextraction and Gas Chromatography," Revision 1.1, EPA Method 504.1, *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III*, EPA-600/R-95-131, NERL, ORD, USEPA, Cincinnati, Ohio, August 1995.

16.2 X-Chrom Reference Manual, LabSystems

16.3 *HP 5890 A Gas Chromatograph Reference Manual Volumes I and II*, Hewlett Packard Company, Avondale, Pennsylvania.

16.4 *HP 7673 Automatic Sampler Operating and Service Manual*, Hewlett Packard Company, Avondale, Pennsylvania.

17.0 Chromatograms, Tables, Diagrams, Flowcharts, and Validation Data

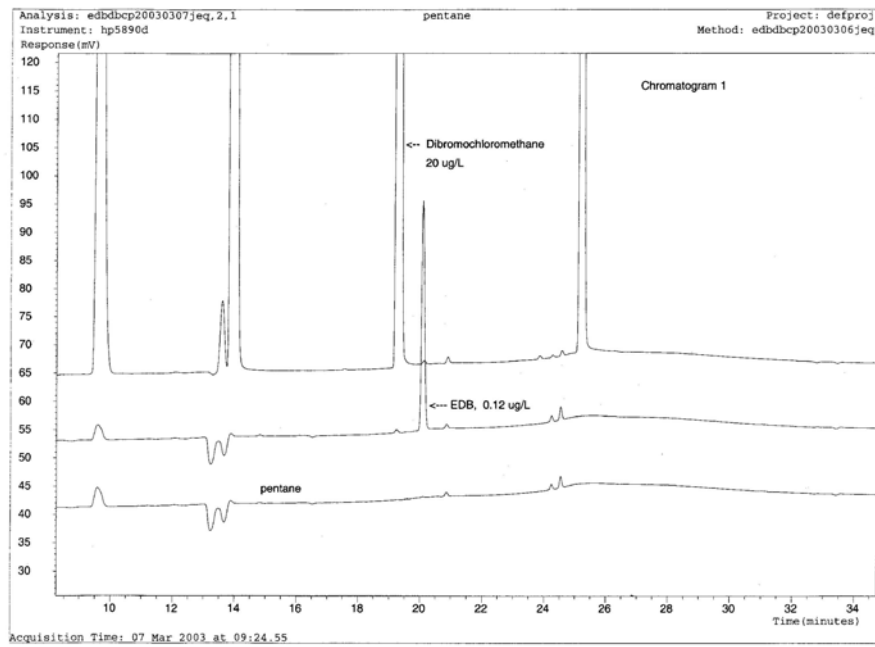


Fig 1

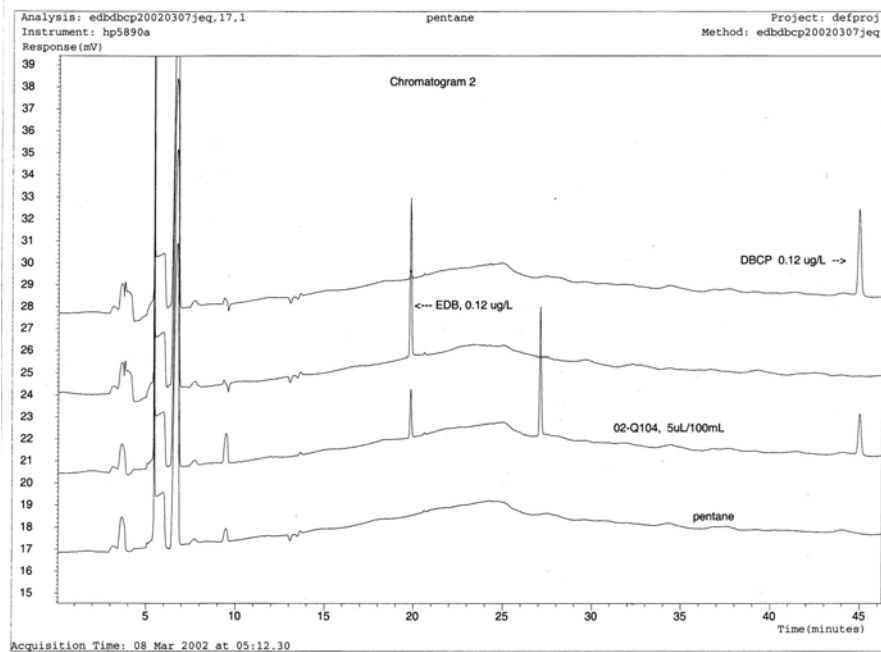


Fig 1

Table 1. Accuracy and Precision Using Column A

| <u>Analytes fortified at 0.10 ug/L</u> | | | | <u>Analytes fortified at 0.20 ug/L</u> | | | |
|--|--------------------------------------|----------------|-------------|--|-------------------------------------|---------------|-------------|
| <u>Replicate #</u> | <u>Recovered Concentration, ug/L</u> | | | <u>Replicate #</u> | <u>Recovered Concentration ug/L</u> | | |
| | <u>EDB</u> | <u>123 TCP</u> | <u>DBCP</u> | | <u>EDB</u> | <u>123TCP</u> | <u>DBCP</u> |
| 1 | 0.1098 | 0.1157 | 0.1093 | 1 | 0.2473 | 0.2175 | 0.2171 |
| 2 | 0.1121 | 0.1090 | 0.1108 | 2 | 0.2640 | 0.2232 | 0.2209 |
| 3 | 0.1109 | 0.1144 | 0.1114 | 3 | 0.2767 | 0.2214 | 0.2160 |
| 4 | 0.1125 | 0.1041 | 0.1118 | 4 | 0.3114 | 0.2186 | 0.2196 |
| 5 | 0.1133 | 0.1101 | 0.1088 | 5 | 0.3146 | 0.2186 | 0.2160 |
| 6 | 0.1228 | 0.1085 | 0.1122 | 6 | 0.2838 | 0.2307 | 0.2162 |
| 7 | 0.1370 | 0.1139 | 0.1090 | 7 | 0.3126 | 0.2258 | 0.2257 |
| mean | 0.1169 | 0.1108 | 0.1105 | mean | 0.2872 | 0.2223 | 0.2188 |
| STD DEV | 0.0098 | 0.0041 | 0.0014 | STD DEV | 0.0266 | 0.0047 | 0.0036 |
| Spk Lev | 0.1000 | 0.1000 | 0.1000 | Spk Lev | 0.2000 | 0.2000 | 0.2000 |
| %Recovery | 116.9 | 110.8 | 110.5 | % Recovery | 143.6 | 111.1 | 109.4 |
| % RSD | 8.41 | 3.69 | 1.28 | % RSD | 9.25 | 2.13 | 1.65 |

Table 2. Accuracy and Precision Using Column B

Analytes fortified at 0.10 ug/L

Recovered Concentration, ug/L

| <u>Replicate #</u> | <u>EDB</u> | <u>123TCP</u> | <u>DBCP</u> |
|--------------------|------------|---------------|-------------|
| 1 | 0.1010 | 0.0718 | 0.0989 |
| 2 | 0.1086 | 0.0915 | 0.1085 |
| 3 | 0.1068 | 0.1091 | 0.1140 |
| 4 | 0.1055 | 0.0894 | 0.1197 |
| 5 | 0.1124 | 0.0920 | 0.1129 |
| 6 | 0.1182 | 0.0835 | 0.1062 |
| 7 | 0.1374 | 0.1060 | 0.1117 |
| mean | 0.1128 | 0.0919 | 0.1103 |
| STD DEV | 0.0121 | 0.0128 | 0.0066 |
| Spk Lev | 0.1000 | 0.1000 | 0.1000 |
| % Recovery | 112.8 | 91.9 | 110.3 |
| %RSD | 10.74 | 13.88 | 5.98 |

Analytes fortified at 0.20 ug/L

Recovered Concentration, ug/L

| <u>Replicate #</u> | <u>EDB</u> | <u>123TCP</u> | <u>DBCP</u> |
|--------------------|------------|---------------|-------------|
| 1 | 0.2361 | 0.1789 | 0.2164 |
| 2 | 0.2486 | 0.1859 | 0.2309 |
| 3 | 0.2784 | 0.2051 | 0.2199 |
| 4 | 0.3099 | 0.1934 | 0.2211 |
| 5 | 0.3138 | 0.1979 | 0.2173 |
| 6 | 0.2641 | 0.2171 | 0.2205 |
| 7 | 0.2924 | 0.1994 | 0.2303 |
| mean | 0.2776 | 0.1968 | 0.2223 |
| STD DEV | 0.0298 | 0.0125 | 0.0059 |
| Spk Lev | 0.2000 | 0.2000 | 0.2000 |
| %Recovery | 138.8 | 98.4 | 111.2 |
| %RSD | 10.7 | 6.36 | 2.65 |